Binuclear Oxovanadium(IV) Complexes as Catalyst for the Oxygenation of the Catechols

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The oxidative cleavage of 3,5-di-t-butyl-1,2-di-hydroxybenzene to give 3,5-di-t-butyl-o-quinone, 3,5-di-t-butyl-1-oxacyclohepta-3,5-diene-2,7-dione, 2,4-di-t-butyl pyron-2-one, is reported. The reaction products were identified by ^1H NMR, IR and mass spectra. The same reaction conditions were employed to oxidize 1,2-dihydroxybenzene and o-phenylene-diamine. In these cases the oxidation products were polymeric and unreacted substrate was recovered at the end of the reaction.

Introduction

Oxidative cleavage reactions of aromatic rings are widespread in nature; typically the enzyme pyrocatechase catalyses the oxidative cleavage of the aromatic ring of catechol to give *cis, cis*-muconic acid [1, 2].

The last decade has seen considerable progress in the understanding of the chemical bonding and structure of various transition metal complexes with oxygen [3–6] and many chemical models for enzymatic oxidations have been discussed [7–10]. The ability of some oxygenases to catalyze oxidative carbon–carbon bond cleavage of various aromatic systems, predominantly phenols and catechols, is well known [9–16].

Most of the reactions are stoichiometric, but even if the reactions are catalytic such activities are very low.

We report here some oxidative non-enzymatic reactions of 3,5-di-t-butyl-1,2-dihydroxybenzene with molecular oxygen activated by binuclear vanadyl(IV) complexes at room temperature.

Experimental

The preparation of the binuclear vanadyl(IV) complexes have been reported [11, 12]. All the solvents were used without purification.

Oxidation of 3,5-Di-t-butyl-1,2-dihydroxybenzene

The oxidation of the substrate was carried out both in air and under oxygen atmosphere.

In Air

A 100 ml flask equipped with a magnetic stirrer, was charged with a 50 ml solution of the catechol (1.11 g, 5 mmol) in CH_2Cl_2. The solution was stirred and then the vanadyl(IV) complex ($5 \cdot 10^{-2}$ mmol) was added. The solution was stirred for 20 h. During this time the reaction was monitored by thin layer chromatography. After this time the reaction mixture was evaporated to dryness and the residue was again monitored on silica gel using chloroform as eluant. Three main fractions were recovered: 3,5-di-t-butyl-o-quinone, muconic acid anhydride and 2H pyran-2-one.

In Oxygen

A CH_2Cl_2 solution of catechol (1.11 g, 5 mmol) and the binuclear vanadyl(IV) complex ($5 \cdot 10^{-2}$

TABLE I. ^{1}H NMR and IR Spectra of Products.[a]

2 H pyran-2-one	^{1}H NMR	1.19 (9H) 1.26 (9H) 6.01 (3H)
m.p. 114–115 °C		
(lit. 113–114 °C [14])	IR	1710 1630 1550 1255 cm^{-1}
Muconic acid anhydride	^{1}H NMR	1.15 (9H), 1.26 (9H), 6.13 (d, 1H), 0.44 (d, 1H)
m.p. 94–95 °C		
(lit. 93–94 °C [15])	IR	1780 1740 cm^{-1}

[a]The ^{1}H NMR spectra were recorded in CDCl$_3$ using (CH$_3$)$_4$Si as internal standard.

TABLE II. Catalytic Oxidation of 3,5-DTBC by Binuclear Vanadyl(IV) Complexes (in CH$_2$Cl$_2$).

Catalyst	Amount of catalyst (%)[a]	Conversion (%)	Products[b]		
			II	III	IV
[VO(acac)OCH$_3$]$_2$	1	100	25	47	10
[VO(tmh)(OCH$_3$)$_2$	1	100	24	46	7
(VOaap)$_2$	1	100	23	48	9
(VOdmba)$_2$	1	100	24	47	8
(VOdba)$_2$	1	100	22	46	10
[VO(acac)OCH$_3$]$_2$[c]	1	100	24	46	9
[VO(acac)OCH$_3$]$_2$[d]	1	100	25	45	8
[VO(acac)OCH$_3$]$_2$[e]	1	100	22	43	9

[a]Based on catechol.   [b]The yield of the isolated products is based on pirocatechol.   [c]In benzene.   [d]In CH$_3$CN.   [e]In chloroform.

tmh = 2,2,6,6-tetramethylheptandione; H$_2$aap = o-hydroxyacetophenone; H$_2$dmba = 1,5-bis(p-methoxyphenyl)-1,3,5-pentane-dione; H$_2$dba = 1,5-diphenyl-1,3,5-pentanetrione.

mmol) was kept at room temperature, in a 100 ml flask. The resulting solution was stirred under oxygen (1 atm) for 20 hrs. After this time the reaction mixture was evaporated to dryness and the residue monitored on silica gel using chloroform as eluant.

Oxygenation of 3,5-Di-t-butyl-o-quinone

The oxygenation of o-quinone was carried out as described in preceeding experiments. After 20 h. unreacted quinone was recovered in quantitative yields.

Oxygenation of 1,2-Dihydroxybenzene

A 100 ml flask was charged with 25 ml of CH$_2$Cl$_2$ and $5 \cdot 10^{-2}$ mmol of the binuclear complex. To the resulting solution was added the catechol dissolved in 25 ml of CH$_2$Cl$_2$. The reaction mixture was stirred for 20 h at room temperature under oxygen atmosphere (1 atm). During this time a black solid was formed. The solution was filtered and the solid washed with CH$_2$Cl$_2$ and dried. The filtrate was evaporated at reduced pressure, the residue dissolved

in CHCl$_3$, and the product separated by column chromatography. Two main fractions were collected: o-quinone and unreacted catechol.

Oxidation of o-Phenylendiamine

The oxidation was carried out as in the preceeding experiment. After 20 h, the 50% of the unreacted diamine was recovered, together with a black polymeric solid.

The oxidative reactions were also carried out in benzene, CHCl$_3$, CH$_3$CN and methanol, using the same reaction conditions.

Results and Discussion

The preparation of the vanadyl(IV) complexes has already been reported [11, 12]; they were characterized by elemental analyses and by their IR, UV spectra. Their magnetic moments are lower than those expected for isolated ions [13], indicating that

an interaction between the vanadyl metal ions is operative.

For [VO(acac)OCH₃]₂ an X-ray crystallographic analysis was carried out [11]. The complex consists of dimeric units, the structure being:
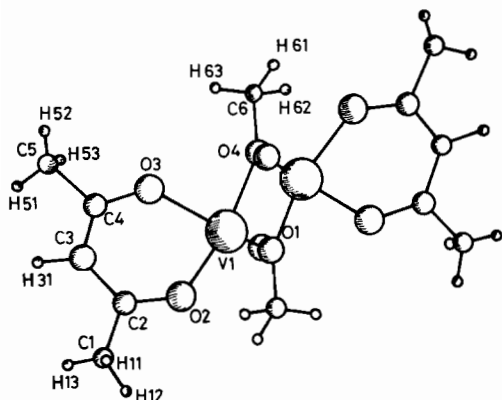

The geometry around the vanadium atom is a tetragonal pyramid, the oxygen atoms are almost planar. The bridging
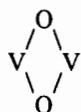
unity is strictly planar, the VO---VO distance being 3.102 Å.

The nature of the species in solution is not certain; it could be that the integrity of the dimer is retained, or that the bridging unit is replaced by the catechol species as a first step in the mechanism, or that a dissociation to a reactive monomer occurs.

The binuclear complexes were dissolved in a 0.1 *M* CH₂Cl₂ solution of 3,5-di-t-butyl-1,2-dihydroxybenzene (3,5-DTBC) (I) and then the reaction mixture was stirred at room temperature under oxygen (1 atm) or air. After two h the 3,5-DTBC disappears and the oxidation products were 3,5-di-t-butyl-*o*-quinone (3,5-DTBQ) (II), muconic acid anhydride (III) and 2 H pyrane-2-one (IV).
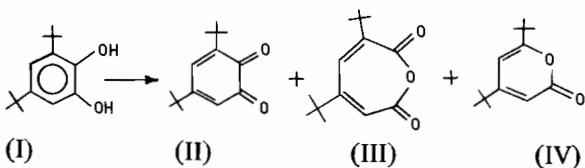
The reaction products were separated by column chromatography on silica gel, using chloroform as eluant; they were recrystallized and characterized

by elemental analyses, IR, ¹H NMR and mass spectra (Table I).

All the investigated complexes were effective for the catalytic oxidation of 3,5-DTBC as shown in Table II. Analogous binuclear copper(II) complexes were examined as catalysts for the oxidation of 3,5-DTBC; in this case only the 3,5-DTBQ was recovered, together with unreacted 3,5-DTBC, and no oxygenated products were determined.

The muconic acid anhydride (III) was obtained directly from 3,5-DTBC and not from (II) as reported [10, 14] for [Cupy(OMe)Cl]₂ and ruthenium complexes. In fact when 3,5-DTBQ was reacted under oxygen (1 atm), using [VO(acac)OCH₃]₂ as catalyst, no oxygenated products were determined after 20 h, the unreacted quinone was completely recovered from the reaction mixture. As solvents CH₃CN, CHCl₃ and benzene can be used, leading to the same products with almost similar yields. Methanol is not a good solvent for these reactions, producing poor yields of (II) even after 20 h.

It is noteworthy in these reactions that there is a high catalytic activity of the binuclear complexes in the oxygenation process (Table II).

Recently it was reported [14] that ruthenium catalyses the oxidation of DTBC to give II, III and IV which arose from an intradiol and extradiol cleavage of the pyrocatechol I respectively, with incorporation of one oxygen atom from molecular oxygen. The muconic acid anhydride was the main product of our reactions (Table II) indicating that the vanadium complexes catalyse intradiol cleavage of the 3,5-DTBC like pyrocatechase. Table II shows that the catechol can be easily oxidized with 1 mol % of the catalyst to give oxidised products in good yields, with high turnover (250) of the catalyst for the oxygenation.

The same results can be obtained when the reactions are carried out in air even if the reaction time is longer than that in an oxygen atmosphere.

The characteristic features of the reactions are as follows:

i) the catechol is oxygenated into the Hamilton intermediate (intradiol type muconic anhydride) and 2 H pyran-2-one (extradiol);

ii) the vanadium complexes show a high catalytic activity;

iii) the oxygenation does not proceed through a *o*-quinone intermediate.

When *o*-di-hydroxybenzene or *o*-phenylendiamine were reacted under the same reaction conditions as above, we were not able to detect the cleavage reaction. From the mixtures black polymeric products were isolated by filtration; moreover from the mother liquor of the catechol reaction *o*-quinone was recovered in poor yields.

Although further systematic studies are necessary to clear the mechanism of the reaction, it is

clear that the vanadium(IV) catalyzed oxygenation is very similar to the pyrocatecase-catalyzed one.

Acknowledgements

References

1 O. Hayashi and K. Hashimoto, *J. Biochem. Tokio, 37*, 371 (1950).
2 G. A. Hamilton, 'Molecular Mechanism of O$_2$ Activation', Ed. O. Haiashi Acc. Press 1974, N.Y.
3 J. H Olive and S. Olive, *Angew. Chem. Int. Ed. English, 11*, 701 (1972).
4 L. A. Vaska, *Acc. Chem. Res., 9*, 175 (1976).
5 J. Valentine, *Chem. Rev., 73*, 235 (1976).
6 F. Basolo, B. M. Hoffmann and J. A. Ibers, *Acc. Chem. Res., 8*, 874 (1975).
7 J. Tsuji and H. Takayanagi, *J. Am. Chem. Soc., 98*, 7349 (1974).
8 J. Tsuji and H. Takayanagi, *Tetrahedron Letters,* 1245 (1975).
9 M. M. Rogic, T. R. Demmin and W. B. Hammond, *J. Am. Chem. Soc., 100*, 5472 (1980).
10 G. Speier and Z. Tyeklar, *J. Mol. Cat., 9*, 233 (1980).
11 M. M. Musiani, F. Milani, R. Graziani, M. Vidali, U. Casellato and P. A. Vigato, *Inorg. Chim. Acta, 61*, 115 (1982).
12 P. A. Vigato, U. Casellato, S. Tamburini, M. Vidali, F. Milani and M. M. Musiani, *Inorg. Chim. Acta, 61*, 89 (1982).
13 B. M. Figgis and J. Lewis, *Progress Inorg. Chem., 6*, 37 (1969).
14 M. Matsumoto and K. Kuroda, *J. Am. Chem. Soc., 104*, 1433 (1982).
15 T. R. Demmin and M. M. Rogic, *J. Org. Chem., 45*, 1153 (1980).
16 T. R. Demmin, M. D. Swerdloff and M. M. Rogic, *J. Am. Chem. Soc., 103*, 5795 (1981).